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RESEARCH ARTICLE

Synthesis, Spectral Characterization and Kinetic Study of Cu(II) Complex with *N*-Hexahydrocyclopenta[*c*]pyrrol-2(1*H*)-yl carbamoyl-4-methylbenzenesulfonamide

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Abstract: Metal complex of anti-diabetic drug, gliclazide was synthesized and characterized using elemental analyses, IR, NMR and thermal analyses technique. The results of conductometric titration using monovariation method indicate that complex is L_2M (2:1) type which was confirmed by Job's method of continuous variation. The complex having the general formula *i.e*. $(C_{15}H_{20}N_3O_3S)_2Cu$. The geometry of complex is assigned square planner supported by IR and ^1H NMR and propose structure (Scheme 2) for complex. The Freeman-Carroll and Sharp-Wentworth methods have been used to calculate activation energy and thermal stability. Thermodynamic parameters such as free energy change (ΔG), entropy change (ΔS) are also determined on the basis of TG curves and by using data of the Freeman-Carroll method and relative thermal stability of the complex are discussed.

Keywords: Gliclazide, Oral anti-diabetic drugs, Gliclazide, Kinetic parameter

Introduction

Gliclazide (Figure 1) is a sulphonylurea derivatives can exist in keto and enolic form when dissolved in an organic solvent and react with various metal ions to form intensely coloured metal complexes that provide the basis for their use as a sensitive reagent. The thermal degradation study of complexes has become a subject of recent interest. It is important property of complexes, which decides the thermal stability and processability of the complexes. The study of thermal behavior of complexes at different temperature provides important information about its practical applicability. Iqbal *et a1*[1]., synthesized the metal complexes of gliclazide characterized by FT-IR, elemental analysis and TGA-DTG parameters. The thermal analysis (TGA) was performed at the heating rate of 10°C/min. in nitrogen atmosphere. Wilma *et al*[2]., studied kinetics and thermal decomposition of Cu(II) complex of hydroxyl quinoline-5-sulphonic acid. Thermal data have been analyzed by Freeman-Carroll and Sharp-Wentworth method. Thermal analysis (TGA and DTG) is a typical analytical technique to describe the relationship between physicochemical changes and temperature[1-2] in order to synthesize complexes having practical applications. There is a need to investigate the effect of heat on complexes in order to establish thermal stability. Iqbal *et al.,*[3-7] have synthesized and characterized complexes of tolbutamide and glibenclamide by FT-IR, elemental analysis and TGA-DTA technique. Thermal studies of complexes were carried out to determine their mode of decomposition, the activation energy (E_a), order of reaction (n), entropy change (ΔS), free energy (ΔF). The Freeman-Carroll and Sharp-Wentworth methods have been used to calculate thermal activation energy and thermal stability. However, very little work has been carried out on the synthesis and characterization and thermal degradation studies of the metal complex of gliclazide. Hence in this work we have prepared the complex of Cu(II) with gliclazide drug. The solid complex was characterized using different physicochemical methods, like elemental analysis (C, H, N, S and metal content), IR, NMR and thermal analysis (TGA and DTG).

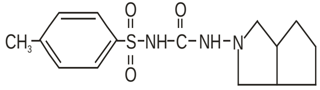

Figure 1. Structure of gliclazide

Experimental

Ligand-metal ratio

a) Gliclazide 0.005 M solution was prepared by dissolving 1.617g in 100 mL ethanol, and cupric chloride solution was prepared by dissolving 0.426 g in 100 mL of ethanol. 10 mL gliclazide solution was titrated conductometrically against cupric chloride solution taken in burette. Conductance was recorded after each addition with proper stirring at temperature 30±1 ^{0}C. Results were plotted between corrected conductance and volume of metal salt. From the equivalent point in the graph, ratio between metal and ligand was noted to be 1:2.

b) Formation of 2:1 (L_2M) ratio was further confirmed by Job's method[8] of continuous variation as modified by Turner and Anderson[9] (Table 1 and Figure 2a & 2b). Spectrophotometric studies were conducted using absorbance as index property, from these values the stability constant (log k) and free energy change (ΔF) were also calculated for gliclazide-copper complex.

Table 1. Gliclazide with copper (Job's method)

S.No.	Metal:Ligand ratio	Absorbance		Corrected Absorbance	
		0.002M	0.005M	0.002M	0.005M
1	0:12	0.006	0.01	0.00	0.00
2	1:11	0.065	0.095	0.059	0.085
3	2:10	0.112	0.135	0.106	0.125
4	3:9	0.167	0.19	0.161	0.175
5	4:8	0.205	0.260	0.198	0.241
6	5:7	0.185	0.240	0.178	0.220
7	6:6	0.145	0.198	0.138	0.185
8	7:5	0.098	0.123	0.090	0.109
9	8:4	0.090	0.112	0.082	0.099
10	9:3	0.052	0.075	0.044	0.065
11	10:2	0.033	0.043	0.025	0.029
12	11:1	0.021	0.025	0.020	0.019
13	12:0	0.009	0.014	0.00	0.00

Synthesis of Complex

The chemicals used in this synthesis were all of Analar Grade Hi-media. A weighed quantity of gliclazide (2 mol) (supplied by Zim laboratory Nagpur, India) was dissolved separately in minimum quantity of 90% ethanol. The cupric chloride solution was prepared by dissolving (1 mole) separately in the same solvent. Ligand solution was added slowly with stirring into the metallic salt solution at room temperature. The pH was maintained between 6.0 and 6.5 by adding dilute NaOH solution. On refluxing the mixture for 3 h and on cooling the complex separated out, filtered off, washed well with ethanol and finally dried in vacuum and weighed.

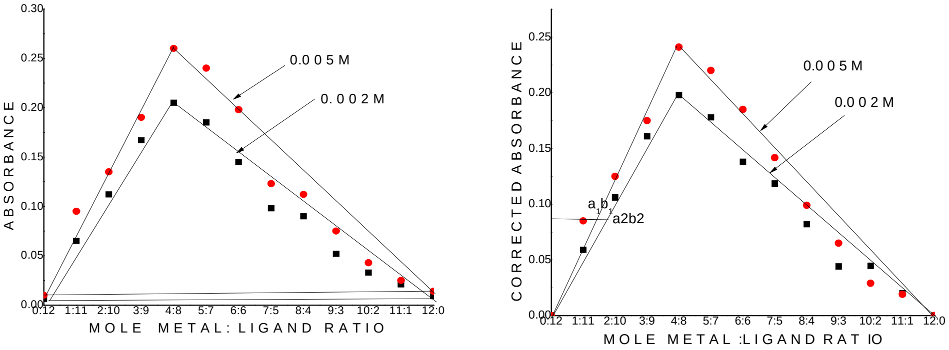

Figure 2a. **Figure 2b**.

Job's Method of continuous variation (Modified by Turner and Anderson)

Instrumentation

The elemental analysis of the isolated complex was carried out using Coleman Analyzer at the Departmental Microanalytical Laboratory CDRI Lucknow. The IR spectra of the ligand as well as of the complex was recorded on Perkin Elemer Spectrometer and ^{1}H NMR spectra of the ligand and isolated complex was recorded on a Bruker DRX-300 spectrometer and d_6-DMSO was used as a solvent. IR and ^{1}H NMR spectra recorded in CDRI, Lucknow and IIT Bombay, India.

From stoichoimetry and analytical data (Table 2), the composition of the complex comes out to be $(C_{15}H_{21}N_3O_3S)_2 \cdot Cu$, for, which favors 2:1 (L_2M) ratio. The tentative structure (*c.f.* Figure 7) was assigned to complex on the basis of analytical data and IR, NMR.

Results and Discussion

Table 2. Analytic and physical data of gliclazide metal complex

S. No.	Complex	Color	Yield %	m.p °C	−ΔF	log K	Molar conductance Ω^{-1} cm^{-1}mole^{-1}
1.	$(C_{15}H_{21}N_3O_3S)_2$ Cu	Maple green	58.79	169	16.65	12.02	30.1
		M. Wt.	Analytical data calculated (theoretical), %				
			C	H	N	S	Metal
		708	50.19 (50.50)	6.00 (6.01)	10.47 (11.47)	9.00 (8.47)	7.99 (7.75)

Infra-Red Spectra Studies

The IR spectra of ligand and isolated complex (Figure 3) were scanned within the range 4000-400 cm^{-1}. Assignments (Table 3) of the infrared spectral bands are based on literature. IR spectrum shows important bands due to ν(M-O) 400-600 cm^{-1}, ν(Ar-S) 700-800 cm^{-1}, ν(-S-N) 1085±20 cm^{-1}, ν(SO_2-N) 1120±20 cm^{-1}, ν(C-N) 1210±20 cm^{-1}, ν(S=O) 1340±20 cm^{-1}, ν(C=O) 1710 cm^{-1}, ν(NH-stretch) 3274±20 cm^{-1}. The proposed structure for the isolated complex is also supported by IR absorption, C.N.Rao[10], Bellamy [11] and Weissberger[12]

^{1}H NMR Studies

^{1}H NMR spectral data are given in Table 4. It is observed that the singlet due to the imide (NH) proton around δ8.033 in the spectrum of the ligand but disappeared in the spectra of NH group in the complex molecule due to formation of M-O band. This is also confirms the deprotonation of imide (NH) group through enolization (the appearance of >C=N stretching band observed in IR spectra). Other features of NMR spectrum were the aromatic presence of unresolved multiplet suggestive protons[13-17].

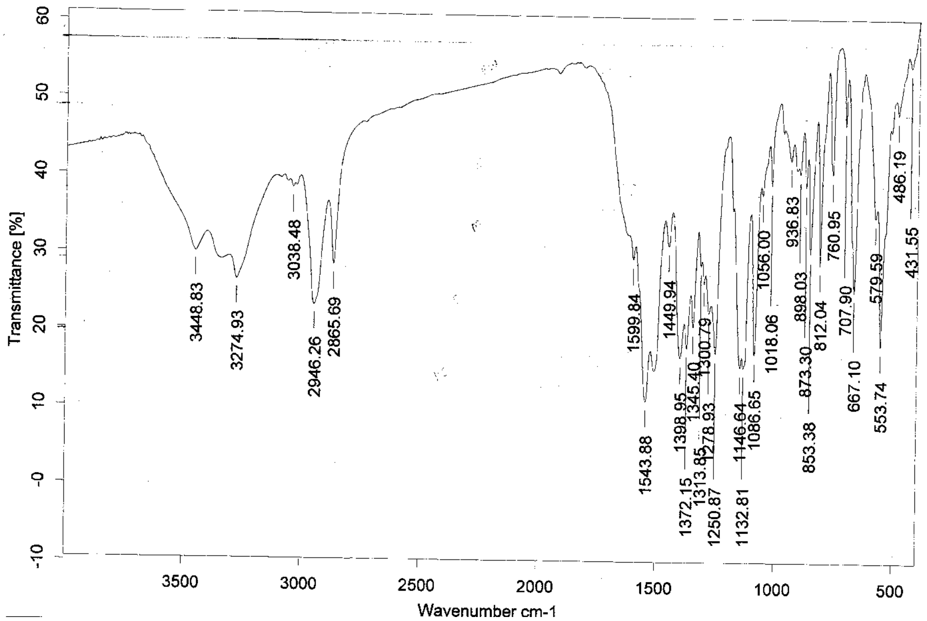

Figure 3. IR spectra of gliclazide-copper complex

Thermal study of gliclazide-copper complex

In the present investigation, the weight loss of the complex was calculated within corresponding temperature ranges. The obtained data are listed in Table 5. The complex is thermally decomposed in three decomposition steps within the temperature range of 50-600 °C. The TGA/DTA curves for the complexes are shown in Figure 4.

Table 3. Specific IR assignment of gliclazide(ligand) and gliclazide-copper complex

Pure drug (Gliclazide)	Gliclazide-Cu complex
632 cm^{-1} (s), 668 cm^{-1} (vs), 1087 cm^{-1} (vs), 1240 cm^{-1} (vs), 1348 cm^{-1} (vs), 1710 cm^{-1} (vs), 2867 cm^{-1}, 2950 cm^{-1} (vs), 3274 cm^{-1} (vs),	547 cm^{-1} (s), 753 (vs), 1122 cm^{-1} (s), 1216 cm^{-1} (vs), 1622 (vs) 1337 cm^{-1} (s), 1524 cm^{-1} (s) 2947 cm^{-1} (m), 3021 cm^{-1} (s), 3674 cm^{-1} (m)
vs = very strong, s = strong	vs = very strong, s = strong, m = medium

Table 4. NMR Assignments of gliclazide-copper complex

$(C_{15}H_{21}N_3O_3S)_2$ pure drug Gliclazide	$(C_{15}H_{20}N_3O_3S)_2Cu$
δ8.041 (s,1H,NHCO, J=0.334Hz), δ7.817 (d, benzene J=1Hz), δ7.395(d, benzene, J=1Hz), δ6.28 (s,SO_2NH), δ3.320 (NH-CO, J=0.929Hz), δ2.901(s,CH_3 group attached to benzene, J=2.160 Hz), δ1.388 (s,CH_3 group, J=2.955Hz	δ7.691 (d,1H,NH-CO, J=1Hz), δ7.346 (d, benzene, J=0.69Hz), δ6.328 (s,SO_2-NH, J=1Hz), δ3.668 (s, NH-CO-Cu, J=0.83Hz), δ2.724 (s,CH_3-group attached to benzene, J=1.26Hz), δ1.608 (q,CH_3 group, J=5.50Hz), δ1.009 (CH_3 group, J=2.03Hz

s=singlet, d=doublet, t=triplet, q=quartrate, m=multiple

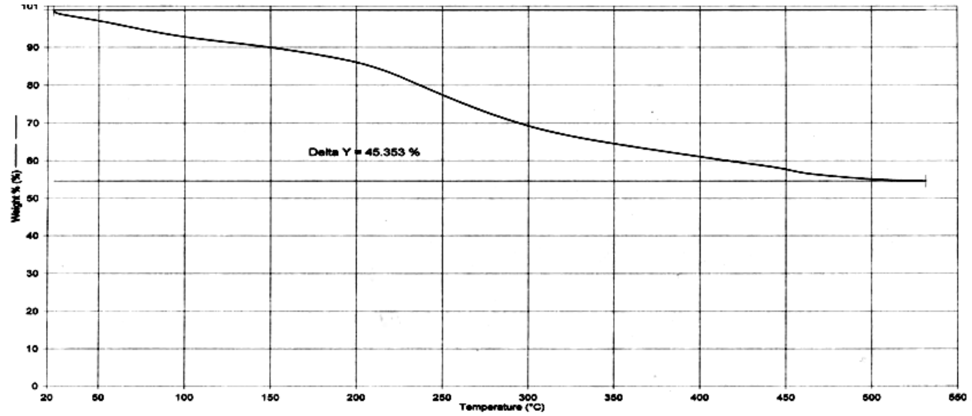

Figure 4. TGA curve of gliclazide -copper complex

The thermoanalytical data are presented in Table 6. In studying the decomposition kinetics methods mentioned in the literature was used in each case the least square plots were drawn. The first few points that did not fall on straight line were discarded. These types of deviations of points are reported in literature by several research workers[20-29].

Theoretical Consideration

To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Freeman-Carroll[27] and Sharp-Wentworth.[28]

Freeman-Carroll Method

The straight line equation derived by Freeman and Carroll is:

$$\frac{\Delta \log \frac{dw}{dt}}{\Delta \log Wr} = n - \frac{Ea}{2.303\,R}\,\frac{\Delta \frac{1}{T}}{\Delta \log Wr}$$

Where, $\frac{dw}{dt}$ = rate of change of weight with time, $Wr = Wc\text{-}W$, $W_c = Wt.$ loss at completion of reaction, W = Total wt. loss up to time 't', E_a = Energy of activation, n = Order of reaction.

The plot between the term $\frac{\Delta \log \frac{dw}{dT}}{\Delta \log Wr}$ *vs* $\frac{\Delta \frac{1}{T}}{\Delta \log Wr}$ gives a straight line (Figure 5) from which slope can be calculated. The energy of activation (E_a) and intercept on Y-axis as order of reaction (n), the change of entropy (ΔS) are also can be calculated.

Sharp-Wentworth Method

Using the Sharp and Wentworth equation:

$$\frac{\Delta \log \frac{dc}{dt}}{(1-c)} = \log \frac{A}{\beta} - \frac{Ea}{2.303R}\,\frac{1}{T}$$

Where, $\frac{dc}{dt}$ = Rate of change of fraction of weight with change in temperature. β = Linear heating rate $\frac{dT}{dt}$, a graph was plotted between $\frac{\Delta \log \frac{dc}{dt}}{(1-c)} vs \frac{1}{T}$. We obtained a straight line (Figure 6) and the energy of activation (E_a) was calculated from its slope.

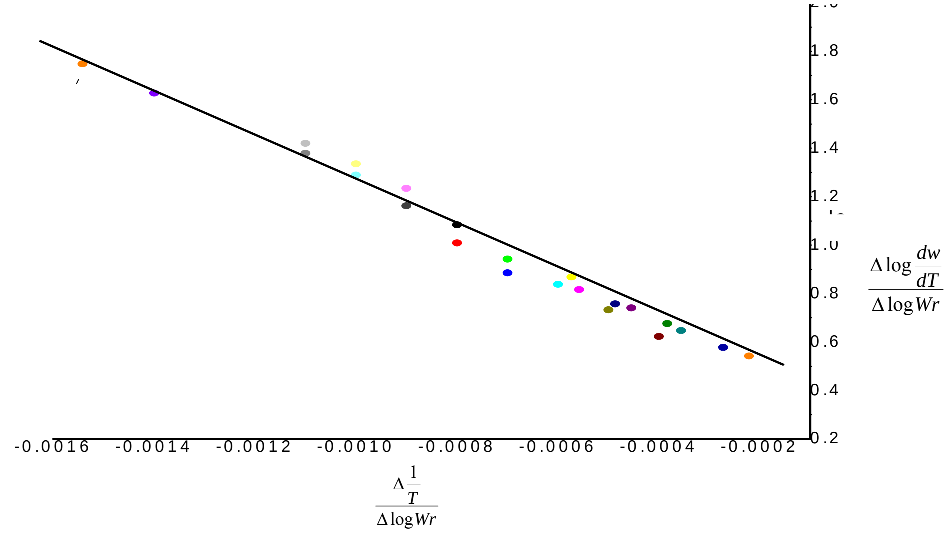

Figure 5. Determination of order of reaction and activation energy by FC method

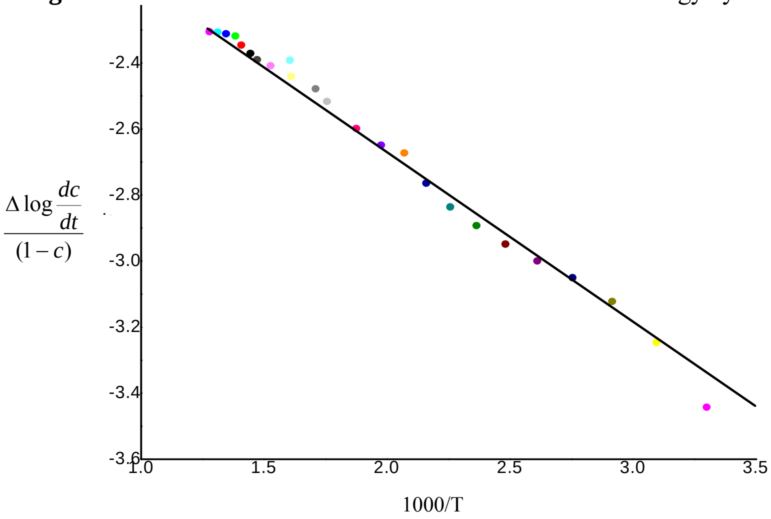

Figure 6. Determination of activation energy by SW method

The thermodynamic activation parameters of decomposition process of dehydrate complexes namely activation energy (E_a), Entropy (ΔS) and Gibb’s free energy change of decomposition (ΔG°) were evaluated graphically by employing Freeman-Carroll and Sharp-Wentworth relation. The data are summarized in Table 7. The activation energies of decomposition are found to be in the range 54 to 56 kJ mole^{-1}. The high value of activation energies reflects the thermal stability of complex. The entropy of activation is found to have negative values in complex which indicate that decomposition reactions process with lower rate than the normal ones**,** beside these parameters, in TGA curve (Figure 5), the initial loss with in temperature 20 – 450 ^{O}C followed by loss of ligand molecule in the next step within the temperature range ≥450 ^{o}C with the formation of metal oxide as a residue of decomposition.

Table 5. Thermogravimetric data of gliclazide metal complex by Sharp-Wenrworth method

Temp. °C	Temp °K	$\frac{1000}{T}$	% Mass Loss	Change in *Wt*. 'c' g	1-c	$\frac{dc}{dt}$	$\log\frac{dc}{dt}$	$\log(1-c)$	$\frac{\log\frac{dc}{dt}}{(1-c)}$	Weight %
30	303	3.30033	1.381	0.00019	0.99981	0.00036	-3.44273	-0.00008	-3.44338	98.619
50	323	3.09598	2.928	0.00040	0.99960	0.00057	-3.24651	-0.00017	-3.24780	97.072
70	343	2.91545	4.752	0.00065	0.99935	0.00075	-3.12209	-0.00028	-3.12411	95.248
90	363	2.75482	6.499	0.00088	0.99912	0.00089	-3.05055	-0.00038	-3.05325	93.501
110	383	2.61097	7.842	0.00107	0.99893	0.00100	-2.99942	-0.00046	-3.00262	92.158
130	403	2.48139	8.928	0.00121	0.99879	0.00113	-2.94832	-0.00053	-2.95191	91.072
150	423	2.36407	10.064	0.00137	0.99863	0.00128	-2.89309	-0.00060	-2.89705	89.936
170	443	2.25734	11.414	0.00155	0.99845	0.00146	-2.83590	-0.00067	-2.84032	88.586
190	463	2.15983	13.007	0.00177	0.99823	0.00172	-2.76460	-0.00077	-2.76951	86.993
210	483	2.07039	15.239	0.00207	0.99793	0.00213	-2.67264	-0.00090	-2.67819	84.761
230	503	1.98807	18.666	0.00254	0.99746	0.00256	-2.59115	-0.00110	-2.59774	81.334
250	523	1.91205	22.575	0.00307	0.99693	0.00295	-2.52985	-0.00134	-2.53764	77.425
270	543	1.84162	26.213	0.00357	0.99643	0.00328	-2.48401	-0.00155	-2.49290	73.787
290	563	1.77620	29.356	0.00399	0.99601	0.00355	-2.45015	-0.00174	-2.45997	70.644
310	583	1.71527	31.94	0.00435	0.99565	0.00374	-2.42724	-0.00189	-2.43783	68.060
330	603	1.65837	33.869	0.00461	0.99539	0.00390	-2.40885	-0.00201	-2.42001	66.131
350	623	1.60514	35.443	0.00482	0.99518	0.00405	-2.39225	-0.00210	-2.40384	64.557
370	643	1.55521	36.875	0.00502	0.99498	0.00420	-2.37703	-0.00218	-2.38901	63.125
390	663	1.50830	38.224	0.00520	0.99480	0.00435	-2.36200	-0.00226	-2.37435	61.776
410	683	1.46413	39.58	0.00539	0.99461	0.00448	-2.34843	-0.00235	-2.36114	60.420
430	703	1.42248	40.865	0.00556	0.99444	0.00464	-2.33339	-0.00242	-2.34643	59.135
450	723	1.38313	42.283	0.00575	0.99425	0.00480	-2.31835	-0.00251	-2.33177	57.717
470	743	1.34590	43.768	0.00596	0.99404	0.00488	-2.31180	-0.00259	-2.32565	56.232
490	763	1.31062	44.602	0.00607	0.99393	0.00493	-2.30734	-0.00264	-2.32143	55.398
510	783	1.27714	45.139	0.00614	0.99386	0.00495	-2.30544	-0.00268	-2.31969	54.861

Table 6. Thermogravimetric data of gliclazide metal complex by Freeman-Corroll method

Temp. °C	% Mass loss	Change in Wt., g	Time, s	$\frac{dw}{dt}$	$\log\frac{dw}{dt}$	$Wr = Wc\text{-}W$	log Wr	T, K	$\frac{1}{T}(K^{-1})$	$\frac{\log\frac{dw}{dt}}{\log wr}$	$\frac{\log\frac{dw}{dt}}{\log wr}$	$\alpha = \frac{wt}{wc}$	$g\alpha = \frac{1-(1-\alpha)^{1-n}}{1-n}$	$T^3 \times 10^{-7}$	$\frac{g(\alpha)}{T^3} 10^7$	$\frac{1}{T} x10^{-3}$	$\log\left(\frac{g(\alpha)}{T^3}\right)$
30	1.381	0.00019	90	0.000389	-3.410	0.00599	-2.2226	303	0.00330	1.534	-0.0015	0.0304	0.0309	2.7818	0.0003	3.3003	-108.8234
50	2.928	0.00040	150	0.000627	-3.203	0.00578	-2.2381	323	0.00310	1.431	-0.0014	0.0645	0.0666	3.3698	0.0013	3.0960	-70.2398
70	4.752	0.00065	210	0.000852	-3.070	0.00553	-2.2572	343	0.00292	1.360	-0.0013	0.1047	0.1104	4.0354	0.0029	2.9155	-48.0044
90	6.499	0.00088	270	0.001023	-2.990	0.00529	-2.2763	363	0.00275	1.314	-0.0012	0.1431	0.1542	4.7832	0.0046	2.7548	-34.6226
110	7.842	0.00107	330	0.001161	-2.935	0.00511	-2.2915	383	0.00261	1.281	-0.0011	0.1727	0.1892	5.6182	0.0058	2.6110	-26.4437
130	8.928	0.00121	390	0.001309	-2.883	0.00496	-2.3043	403	0.00248	1.251	-0.0011	0.1966	0.2185	6.5451	0.0066	2.4814	-20.8855
150	10.064	0.00137	450	0.001485	-2.828	0.00481	-2.3180	423	0.00236	1.220	-0.0010	0.2216	0.2500	7.5687	0.0073	2.3641	-16.6010
170	11.414	0.00155	510	0.001692	-2.772	0.00462	-2.3349	443	0.00226	1.187	-0.0010	0.2514	0.2887	8.6938	0.0083	2.2573	-13.1039
190	13.007	0.00177	570	0.001985	-2.702	0.00441	-2.3558	463	0.00216	1.147	-0.0009	0.2865	0.3364	9.9253	0.0097	2.1598	-10.2373
210	15.239	0.00207	630	0.002436	-2.613	0.00410	-2.3868	483	0.00207	1.095	-0.0009	0.3356	0.4072	11.2679	0.0121	2.0704	-7.6705
230	18.666	0.00254	690	0.002945	-2.531	0.00364	-2.4391	503	0.00199	1.038	-0.0008	0.4111	0.5267	12.7264	0.0170	1.9881	-5.2213
250	22.575	0.00307	750	0.003413	-2.467	0.00311	-2.5078	523	0.00191	0.984	-0.0008	0.4972	0.6828	14.3056	0.0237	1.9120	-3.2795
270	26.213	0.00357	810	0.003816	-2.418	0.00261	-2.5831	543	0.00184	0.936	-0.0007	0.5773	0.8538	16.0103	0.0308	1.8416	-1.9191
290	29.356	0.00399	870	0.004146	-2.382	0.00218	-2.6608	563	0.00178	0.895	-0.0007	0.6465	1.0292	17.8454	0.0373	1.7762	-0.9913
310	31.94	0.00435	930	0.004391	-2.357	0.00183	-2.7371	583	0.00172	0.861	-0.0006	0.7034	1.2009	19.8155	0.0426	1.7153	-0.3698
330	33.869	0.00461	990	0.004592	-2.338	0.00157	-2.8042	603	0.00166	0.834	-0.0006	0.7459	1.3515	21.9256	0.0460	1.6584	0.0161
350	35.443	0.00482	1050	0.004776	-2.321	0.00136	-2.8679	623	0.00161	0.809	-0.0006	0.7806	1.4941	24.1804	0.0482	1.6051	0.2762
370	36.875	0.00502	1110	0.004950	-2.305	0.00116	-2.9353	643	0.00156	0.785	-0.0005	0.8121	1.6444	26.5848	0.0502	1.5552	0.4726
390	38.224	0.00520	1170	0.005125	-2.290	0.00098	-3.0101	663	0.00151	0.761	-0.0005	0.8418	1.8106	29.1434	0.0523	1.5083	0.6281
410	39.58	0.00539	1230	0.005291	-2.276	0.00079	-3.1010	683	0.00146	0.734	-0.0005	0.8717	2.0119	31.8612	0.0550	1.4641	0.7657
430	40.865	0.00556	1290	0.005475	-2.262	0.00062	-3.2092	703	0.00142	0.705	-0.0004	0.9000	2.2505	34.7429	0.0583	1.4225	0.8823
450	42.283	0.00575	1350	0.005667	-2.247	0.00042	-3.3718	723	0.00138	0.666	-0.0004	0.9312	2.6067	37.7933	0.0642	1.3831	1.0191
470	43.768	0.00596	1410	0.005771	-2.239	0.00022	-3.6522	743	0.00135	0.613	-0.0004	0.9639	3.2148	41.0172	0.0756	1.3459	1.1975
490	44.602	0.00607	1470	0.005838	-2.234	0.00011	-3.9616	763	0.00131	0.564	-0.0003	0.9823	3.8765	44.4195	0.0857	1.3106	1.3073
510	45.139	0.00614	1530	0.005871	-2.231	0.00004	-4.4414	783	0.00128	0.502	-0.0003	0.9941	4.8845	48.0049	0.1012	1.2771	1.4296

Table 7. Thermal analyses result of gliclazide complex.

Complexes	Decomposition Temp. °C	%Wt. loss	E_a, J/mole F.C.	S.W.	ΔS J/k/mole	ΔG kJ/mole	n
$(C_{15}H_{20}N_3O_3S)_2Cu$	40-510	45	54.89	56.48	-77.31	23.08	0.55

For supporting the proposed structure of copper-gliclazide complex, initially Job's method of continuous variation as modified by Turner and Anderson was conducted which indicate 2:1 ligand:metal ratio of the complex, moreover stability constant and free energy change was also calculated. Analytical data (*c.f.* Table 2) agrees to the molecular formula $(C_{15}H_{20}N_3O_3S)_2Cu$. Thermal analysis of complex has been studied by giving their relative thermal stability. Applying the Sharp-Wentworth and Freeman–Corroll methods energy of activation (E_a), kinetic parameter *viz.* ΔS, ΔG and order of reaction (n) were determine by applying Freeman-Corroll method.

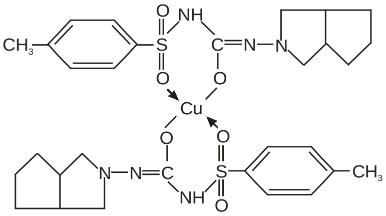

Figure 7. Proposed structure for gliclazide-copper complex

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